

Attorney Docket No. 2002B147/2

**REMARKS/ARGUMENTS**

Entry of the foregoing and further consideration of the subject application in light of the remarks that follow and consistent with 37 C.F.R. 1.114 are respectfully requested.

Claims 1-74 are pending in the current application. Claims 50-57 and 71-74 have been withdrawn from consideration by the Examiner. No claim amendments are made in the current response. Paragraph 00105 of the Application has been amended to correct a typographical error.

No new matter has been added.

**CLAIM REJECTIONS – 35 U.S.C. § 102(e)**

Claims 1-41 have been rejected under 35 U.S.C. § 102(e) as unpatentable over U.S. Patent No. 6,583,227 to Mehta, *et al.* ("Mehta"). Applicants request reconsideration of this rejection in light of the following statements.

Page 3 of the Office Action states, "... the Examiner contends that broad, bimodal molecular distribution as stated in Mehta is synonymous with unimodal distribution found in the claimed invention." By its very nature, unimodal molecular weight distribution ("MWD") is not synonymous with bimodal MWD. A polymer's unimodal molecular weight distribution depicted graphically, results in a smooth curve with a single peak (and consequently, a single inflection point). In contrast, a bimodal MWD, no matter how broad, is a curve with at least two peaks (and thus, at least two inflection points). This is shown graphically in Mehta at Fig. 6. Mehta distinguishes its invention (examples 10 and 11), polymers with broad, bimodal MWD curves, from that of "control samples" (examples 12-18), which exhibit unimodal MWD curves. *See* Mehta at Fig. 6.

Further, it is well known in the art that unimodal and bimodal molecular weight distributions are not "synonymous" as claimed by the Examiner. The following is a description of the known differences between unimodal and bimodal molecular weight distribution:

By the "modality" of a polymer is meant the structure of the molecular-weight distribution of the polymer, i.e. the appearance of the curve indicating the number of molecules as a function of the molecular weight. If the curve exhibits one maximum, the polymer is referred to as "unimodal", whereas if the curve exhibits a very broad maximum or two or more maxima and the polymer consists of two or more fractions, the polymer is referred to as "bimodal", "multimodal" etc.

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See PCT International Publication No. WO 99/65039, *An Insulating Composition for Communication Cables*, p. 5., lns. 6-14; see also Virendrakumar Gupta, C.P. Vinod, G.U. Kulkarni, Goutam K. Lahiri, Niladri Maity and Sumit Bhaduri, *Polyethersulfone supported titanium complexes as ethylene polymerization catalysts*, 88 CURRENT SCIENCE No. 7, 1163-64 (April 10, 2005) (describing Figure 1 as depicting a unimodal polymer, identified by "(1)", and a bimodal polymer, identified by "(3)", a copy of which is attached as Exhibit 1.

In light of the above, Applicants respectfully request the rejection be withdrawn and the Application proceed to Allowance.

### CONCLUSION

It is respectfully submitted that all pending claims are in condition for allowance. Accordingly, Applicants request early and favorable reconsideration in the form of a Notice of Allowance.

If necessary to affect a timely response, this paper should be considered as a petition for an Extension of Time sufficient to affect a timely response. Please charge any deficiency in fees or credit any overpayments to Deposit Account No. 05-1712 (Docket #: 2002B147/2).

Respectfully submitted,



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May 9, 2006

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**ACKNOWLEDGEMENTS.** We thank Prof. V. Singh (NEHU, Shillong) for valuable assistance in the experimental work and Dr S. Agarwal (DMSRDE, Kanpur) for analysis of synthesized materials.

Received 14 June 2004; revised accepted 18 January 2005

## Polyethersulfone supported titanium complexes as ethylene polymerization catalysts

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Polyethersulfone has been used as the support to anchor  $TiCl_4$  or  $Cp_2TiCl_2$  through dative 'O-Ti' bond. The supported complexes in combination with methylaluminoxane are effective ethylene polymerization catalysts. The polyethylene made by the supported catalysts, especially the titanocene-derived catalyst, has low polydispersity indicating single site character.

NOVEL catalysts for the manufacture of polyethylene are of great current research interest<sup>1</sup>. While most of the commercial heterogeneous catalysts are based on silica-supported chromium, or magnesium chloride-supported titanium species, in recent years metallocene and non-metallocene transition metal complexes, the so-called single site catalysts, have attracted significant attention<sup>1,2</sup>.

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From the point of view of practical application anchoring of catalytically active titanium complexes onto a suitable support, by a simple synthetic procedure, and with minimum alteration of the ligand environments is a challenge<sup>3,4</sup>. The supported catalyst at the molecular level must be well-defined and when used in polymerization reactions, should approximate single-site behaviour.  $TiCl_4$  and  $Cp_2TiCl_2$  are two of the most easily available and widely used precursors for magnesium chloride-supported Ziegler-Natta and single-site metallocene catalysts respectively. Thus from the point of view of potential application, it is highly desirable to find a polymer that without functionalization is capable of tethering  $TiCl_4$  and titanium metallocene complexes through well-defined chemical bonds. Unlike other supported homogeneous catalysts, the purpose of anchoring is therefore not the easy separation of the catalyst, but to impart single site character to a supported catalyst. Furthermore such supported catalysts can be easily used in fluidized bed reactors.

In this communication we report that polyethersulfone (PES) is a versatile support material on which  $TiCl_4$  and  $Cp_2TiCl_2$  could be easily anchored through dative 'O-Ti' bond. The supported complexes in combination with methylaluminoxane (MAO) are effective ethylene polymerization catalysts. The polyethylene made by the supported catalysts, especially the titanocene-derived catalyst, has low polydispersity indicating single site character.

Triethylaluminum ( $AlEt_3$ ) (Scherings, AG, Germany), titanium tetrachloride ( $TiCl_4$ ) (Merck, Germany) and bis(cyclopentadiene) titanium dichloride ( $Cp_2TiCl_2$ ) (Aldrich, USA) were used as received without further purification. Polyethersulfone (average  $M_n \sim 20,000$ ) was a gift sample from Gharda Chemicals, India. All operations unless stated otherwise were carried out under an inert atmosphere of nitrogen or argon. GPC chromatograms (140°C, trichlorobenzene as solvent) were recorded on a Polymer Laboratory 220 instrument.

A solution of  $Cp_2TiCl_2$  (1.7 GM) in dichloromethane (20 cm<sup>3</sup>) is added drop wise under nitrogen to a dichloromethane (200 cm<sup>3</sup>) solution of PES (5 GM) at 25°C and stirred for 2 h. Pale yellowish precipitate of 1 separates out from the clear solution, which is isolated by filtration and washed repeatedly with dichloromethane and stored under dry nitrogen. This material is used for all subsequent experiments with 1.

Catalyst 2 is prepared and isolated by a similar procedure by using  $TiCl_4$  (1.3 GM) and PES (5 GM). Catalyst 4 is prepared by mixing dichloromethane solutions (100 cm<sup>3</sup> each) of  $TiCl_4$  (1.3 GM) and dimethyl sulfone (0.1 GM), stirring the solution for 4 h, removing the solvent under reduced pressure and washing the residue with toluene (1 ml) and hexane.

All polymerization experiments were carried out in a double-jacketed three-necked glass reactor of one-litre capacity, in toluene (200 ml) at 27°C for 60 min. In all the experiments the cocatalyst used was MAO (30%), the amount of

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catalyst used was between 0.05 to 0.5 GM and an Al:Ti molar ratio of 100:1 was maintained. For polymerization with 3, the catalyst was prepared *in-situ* by mixing  $\text{Cp}_2\text{TiCl}_2$  (0.37 GM) and  $\text{Me}_2\text{SO}_2$  (0.09 GM) and allowing the solution to equilibrate for 2 h before initiating polymerization by the addition of MAO and ethylene.

Reactions of PES with  $\text{Cp}_2\text{TiCl}_2$  and  $\text{TiCl}_4$  lead to the formation of 1 and 2 respectively. The tentative formulations of the supported species (Scheme 1) are based on analytical and XPS data. By adjusting the relative amount of PES and the precursor titanium complex, the amount of titanium loading in the supported species could be controlled. Optimum catalytic activity is observed for titanium contents between 3 and 5%.

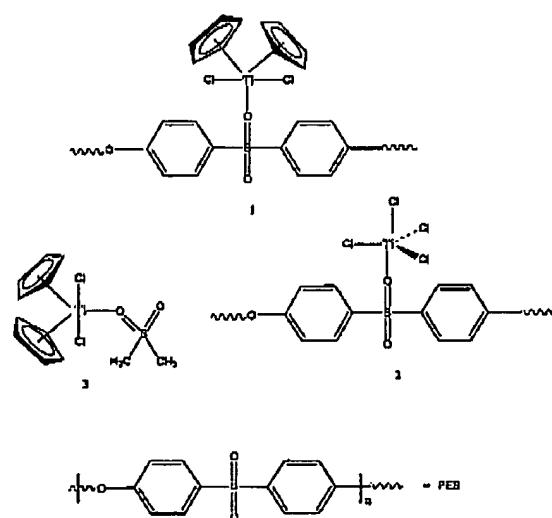
In 1 and 2 the Ti:Cl molar ratios are found to be 1:2 and 1:4 respectively. In PES the XPS signal corresponding to sulfur 2p (spin-orbit unresolved) is observed as a broad feature centered at  $\sim 170$  eV (Au 4f<sub>7/2</sub> as reference at 84.0 eV). However, in both 1 and 2 the sulfur peak could be deconvoluted into two peaks (spin-orbit unresolved) of binding energies 173.5 and 170 eV. It is reasonable to ascribe the peak of binding energy 173.5 eV to the sulfur atoms of those sulfone groups that have oxygen atoms co-ordinated to  $\text{Ti}^{4+}$ . For 2, the titanium spin-orbit doublet,  $2p_{3/2}$  and  $2p_{1/2}$  appear at 458.5 and 465.5 eV, while the peak due to chlorine 2p appears at 200 eV. These values are close to that of the literature reported data<sup>5</sup> for  $\text{TiCl}_4$  on  $\text{MgCl}_2$ .

By reacting  $\text{Cp}_2\text{TiCl}_2$  and  $\text{TiCl}_4$  with molar amounts of  $\text{Me}_2\text{SO}_2$  we attempted the syntheses and isolation of the model complexes  $\text{Cp}_2\text{TiCl}_2(\text{Me}_2\text{SO}_2)$  3, and  $\text{TiCl}_4\cdot\text{Me}_2\text{SO}_2$  4, respectively. While the addition of  $\text{Me}_2\text{SO}_2$  to an orange

solution of  $\text{Cp}_2\text{TiCl}_2$  does lead to a slight colour change, all attempts to isolate 3 as a solid have been unsuccessful. At the end of the reaction, unreacted  $\text{Cp}_2\text{TiCl}_2$  and  $\text{Me}_2\text{SO}_2$  are recovered. This indicates that 3 is stable in solution, and its isolation as a solid is not possible due to the labile bonding of  $\text{Me}_2\text{SO}_2$  with  $\text{Cp}_2\text{TiCl}_2$ . In contrast, complex 4 can be isolated as a moisture and air-sensitive orange yellow microcrystalline solid. The analytical data (Ti, Cl, C, H) of 4 are consistent with the proposed formulation. In 4 the  $935\text{ cm}^{-1}$  band of dimethylsulfone is replaced with a band at  $\sim 900\text{ cm}^{-1}$ . The electrospray ionization mass spectrum of 4 has a molecular ion peak at 284 mass number.

Attempts to grow single crystals of 4 for X-ray structure determination have so far been unsuccessful. However, as shown in Figure 1a, on the basis of density functional (DFT) calculations at B3LYP/LANL2DZ level, the minimum energy structure of 4 is expected to be a slightly distorted trigonal bipyramidal. Examples of co-ordination complexes where DMSO as one of the ligands co-ordinates either through oxygen or sulfur atom are known<sup>6</sup>. In the DFT predicted structure, dimethylsulfone co-ordinates through an oxygen atom and acts as a monodentate ligand. Preliminary DFT calculations predict a similar structure and co-ordination environment also for 3.

The catalytic activities of 1-4 have been evaluated for ethylene polymerization (Table 1), and not for any co-polymerization reactions involving other 1-alkenes. The



Scheme 1. Proposed formulations of 1, 2 and 3. DFT based structure of 4 is given in Figure 1a.

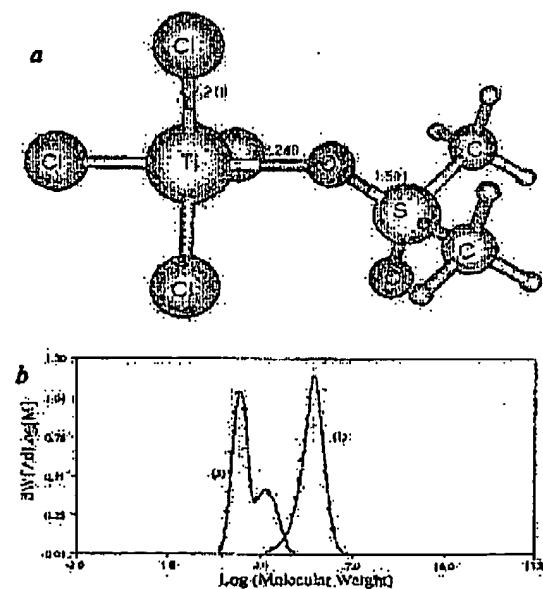


Figure 1. a, DFT (B3LYP/LANL2DZ) predicted structure of 4; b, Molecular weight distribution of polyethylene obtained by using 1 and 3 as the catalysts.

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Table 1. Evaluation of 1-4 as polyethylene catalysts and polymer properties

Catalyst	Activity* (kg PE/moleTi/h/bar)	M <sub>n</sub> ** (x 10 <sup>5</sup> )	Polydispersity**
1	1600	3.1	2.1
2	40	2.7	4.5
3	25.9	0.27	Bimodal
4	11.5	0.33	22.7

\*All catalytic runs carried out in toluene (200 ml) at 298 K under 1 bar ethylene for 1 h with MAO as the cocatalyst (Al : Ti is 100 : 1).

\*\*Measured by high temperature GPC with polyethylene as standard.

number of average molecular weights of polyethylene obtained with 1 and 2 is approximately one order of magnitude higher than those obtained with 3 and 4. There is a notable reduction in the polydispersity of the polymers obtained with 1 and 2 as the catalysts, compared to those obtained by using 3 and 4. As shown in Figure 1 b, a broad and distinctly bimodal molecular weight distribution function, a characteristic feature of many multisite catalysts is obtained for 3. However with 1, a narrow unimodal molecular weight distribution function is obtained.

When combined with the cocatalyst, complexes 3 and 4 like the well-established first generation Ziegler–Natta system are expected to give rise to *multisite colloidal* catalysts resulting in the formation of polymers with high polydispersity. On the other hand, majority of the surface catalytic sites in the supported catalysts have identical structures. These species are therefore expected to behave more as single site catalysts giving polymers of comparatively low polydispersity<sup>2b,7</sup>.

Polymerization reactions where MAO is used as the co-catalyst have been reported to involve the cleavage of metal alkoxide bonds<sup>8</sup>. It is very likely that with 1 and 2, cleavage of some of the dative Ti–O bonds does take place and as the reaction proceeds some of the anchored titanium species are leached out of the support. However, the leached out dissolved species, as well as 2, 3 and 4 probably undergo quick deactivation. In contrast, the diffusion barrier between the solution and the insoluble support, and the steric crowding in Cp<sub>2</sub>TiCl<sub>2</sub> make the supported catalytic species of 1 resistant towards deactivation. This would explain why the molecular weight of polymer obtained with 1 is notably higher than that of all the others.

In conclusion, we have shown that PES is versatile support material for polymerization catalysts. Complexes Cp<sub>2</sub>TiCl<sub>2</sub> and TiCl<sub>4</sub> can be supported on PES through dative O–Ti bonds. The supported materials in combination with MAO give polymers of low polydispersity indicating single site behaviour.

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ACKNOWLEDGEMENTS. Experimental assistance of M. V. Birajdar and B. J. Modi, useful discussions with Dr S. Kulkarni, constructive comments from the referee and financial assistance from Reliance Industries Limited, are gratefully acknowledged.

Received 12 October 2004; revised accepted 19 January 2005

## Cloning of synthetic VP2 gene of infectious bursal disease virus in a mammalian expression vector and its use as DNA vaccine in chicken

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The 1367 bp VP2 gene of infectious bursal disease virus was synthesized in three phases and cloned in pUC18 vector. All the three clones having the inserts were bidirectionally sequenced and minor mutations were repaired. The three selected clones were sequentially cloned in pUC29 vector. The 1367 bp gene was released from the pUC29 and recloned in pVAX1 vector. The recombinant plasmid was designated as pVAX1.ibdvp2. It was used to transfect chick embryo fibroblast culture and found to express VP2 protein, as detected by immunoperoxidase test. The recombinant plasmid was used as DNA vaccine in chicken using 50 µg per chick, injected intramuscularly. It was found to give 100% protection, while vector inoculated or healthy control chicken died/suffered from the disease. The present work showed that the recombinant plasmid can be used as DNA vaccine against infectious bursal disease in chicken.

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